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Transformation to a tetragonal structure of filled ice Ic hydrogen hydrate under low temperature and high pressure

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1 Introduction

Hydrogen hydrates have been reported to be potentially ubiquitous in space as icy bodies. Also, one type of hydrogen hydrates, i.e. the clathrate structure, has recently received significant interest as an environmentally clean hydrogen storage material. A high-pressure phase of hydrogen hydrate takes a filled ice Ic structure [1] (referred to as HH-C2). The host framework of HH-C2 is a diamond-like structure similar to ice Ic, in which hydrogen molecules (guest) occupy small voids in the host ice framework. The host ice framework of HH-C2 is similar to that of ice Ic described above; thus, HH-C2 is thought to have a cubic structure. However, a recent theoretical study using first principle calculations predicted that the cubic structure of HH-C2 transforms to tetragonal under high pressure and low temperature [2].

In this study, low-temperature and high-pressure experiments were performed to clarify the phase changes of HH-C2 in the previously unexplored region from 5 to 50 GPa at 30 to 300 K. This will confirm the existence of the theoretically predicted tetragonal phase and determine the range of conditions that support its presence.

2 Experiment

Clamp-type diamond anvil cells and a helium-refrigeration cryostat were used to attain high pressure and low temperature conditions, respectively. Re gaskets were used to avoid reactions with H_2. Pressure measurements were made via the ruby fluorescence method and the diamond Raman method using an on-line measurement system. Temperature measurements were made using a silicon semiconductor thermometer and chromel-alumel thermocouples. The initial samples were prepared by gas-loading method. The samples were characterized via X-ray diffractometry (XRD) at BL-18C at the Photon Factory (KEK).

3 Results and Discussion

Below 20 GPa, all diffraction lines were indexed as the HH-C2 cubic structure. Above 20 GPa, the 220, 311, 400, and 331 diffraction lines that describes the cubic structure began to split to a higher angle; these splitting diffraction lines were indexed as 220 and 202, 311 and 113, 400 and 004, and 331 and 313 for the tetragonal structure. While, the 111 diffraction line did not split at these conditions. Similar splitting of the lines were observed at low temperature region. Therefore, the XRD study revealed that the cubic filled ice Ic structure transformed to a tetragonal at over a wide low-temperature and high-pressure region. From the distribution of the cubic and tetragonal structures, the boundary between the two structures can be inferred to exist along the points at ~20 GPa and 300 K, 15 GPa and 200 K, and 10 GPa and 100 K (dashed line in Figure 1). Above 40 GPa, another high-pressure phase was observed, which is consistent with our previous study [3].

A possible reason for the formation of the tetragonal structure is discussed below. A candidate for the reason is symmetrization of hydrogen bonds of host framework as inferred in the previous study [3]. However, in the present experiments the tetragonal structure was observed at very low pressure, even at 10 GPa at 100 K. If the tetragonal structure is induced by symmetrization, of hydrogen bond the present results imply that this occurs at very low pressures in the low temperature region. At such low pressures, the oxygen–oxygen distance is much longer than that expected for symmetrisation of hydrogen bond. Therefore, there must be a more reasonable explanation for the change to the tetragonal structure. The vibrational modes of the hydrogen molecules in the cubic HH-C2 structure are thought to be rotating freely with spherical symmetry at ambient conditions. Change in the rotational modes of the hydrogen molecules from spherical to asymmetrical one is likely to be induced at low temperature and high pressure. Such change might result in deformation of the cubic lattice to a tetragonal one.

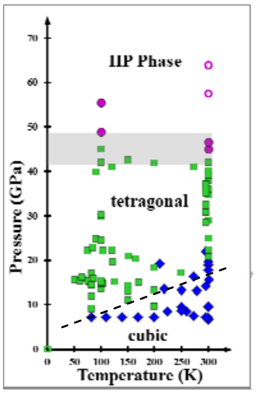

Fig. 1: Phase changes.

References

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